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DEVELOPMENT OF HIGH-DIELECTRIC-CONSTANT, LOW-DIELECTRIC-LOSS POLYMERS UTILIZING GAMMA IRRADIATION

INTRODUCTION TO PART V

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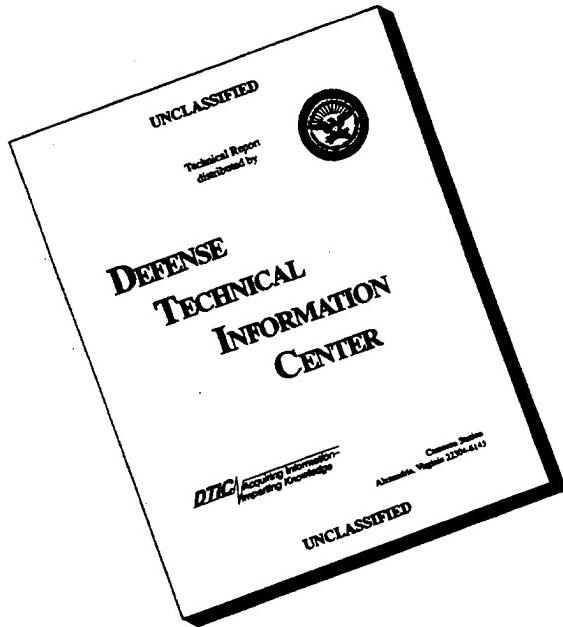
Prepared for

**UNITED STATES ATOMIC ENERGY COMMISSION
DIVISION OF ISOTOPES DEVELOPMENT**

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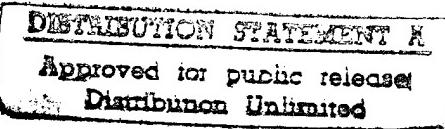
by

Manfred Luttinger
Francis A. Sliemers, Jr.
John F. Kircher
Robert I. Leininger

Topical Report
on a Study for

UNITED STATES ATOMIC ENERGY COMMISSION
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DEVELOPMENT OF HIGH-DIELECTRIC-CONSTANT,
LOW-DIELECTRIC-LOSS POLYMERS UTILIZING GAMMA IRRADIATION

Manfred Luttinger, Francis A. Sliemers, Jr.,
John R. Kircher, and Robert I. Leininger

(The polymerization of methyl methacrylate, β -cyanoethyl acrylate, ethyl vinyl sulfone, and β -trifluoroethyl vinyl ether and the copolymerization of β -cyanoethyl acrylate and ethyl vinyl sulfone were investigated for optimum polymer production and purity by radiation and chemical catalytic methods. Dielectric constants and dissipation factors were determined, but no significant difference between the dielectric properties of free-radical polymerized polymers prepared by γ -radiation or by chemical catalysts was discovered. The polymerization of ethyl vinyl sulfone proceeded only with great difficulty, and only moderate yields of low-molecular-weight polymers were obtained. The copolymerization of ethyl vinyl sulfone and β -cyanoethyl acrylate did not improve the yields materially, but resulted in a small increase in molecular weights. The dependence of the dielectric constant on the glass transition temperature in the homopolymers and copolymers of these two monomers was defined. β -Trifluoroethyl vinyl ether was polymerized by γ -radiation below room temperature at a dose rate of 5×10^5 rep per hr and a total dose of 1.6×10^7 rep. The attempted radiation polymerization of some allylic monomers, both in the solid and in the liquid state, was unsuccessful.)

INTRODUCTION

The objective of this investigation was to evaluate the usefulness of radiation polymerization techniques in the development of high-purity plastics and to compare the resulting polymers with similar polymers prepared with chemical catalytic methods. Radiation polymerization was expected to lead to improved materials free from the catalyst residues found in polymers prepared with chemical initiators. Radiolysis products were believed to be insignificant at the low doses required for the polymerization of most monomers readily susceptible to free-radical catalysis.

The development of high-purity polymers free from polar residues is of particular interest to the electronics industry, both in the field of insulation materials, where nonpolar compounds are of interest, and in the field of electroluminescence, where highly polar materials are required. The latter area has been receiving considerable attention in recent years, with low-level electroluminescent light sources already on the market and the introduction of panels for room lighting expected in the foreseeable future. Electroluminescent devices for computers, instruments, and television applications are also under development. The present program was designed to contribute to the development of materials having the high standards of purity required for these applications through radiation polymerization. Any improvement in polymer purity may also be of interest for high-voltage insulation.

Embedding materials for electroluminescence must have a high dielectric constant to transmit the electrical energy to the phosphors. The brightness of an electroluminescent light panel, for instance, is a function of the ratio of the dielectric constants of the embedding material and of the phosphors. At the same time, the useful life and the efficiency of operation of a device is dependent on a low loss factor, which is the product of the dielectric constant and the dissipation factor. The most desirable material should, therefore, have a high concentration of strongly polar groups which are free to orient themselves in an alternating electrical field and should also be as free from polar and ionic residues as is possible. It was believed that radiation polymerization could be economically attractive, if the need for expensive purification procedures were reduced.

EXPERIMENTAL WORK

Laboratory and Testing Procedure

Purity is of special importance in studying the dielectric properties of polymers. In the work reported here, monomers, solvents, and precipitants were dried to eliminate even small quantities of water, which is one of the critical impurities. Volatile solvents were preferred over less volatile ones, and, wherever possible, nonpolar reagents were used. The finished products were subjected to extended drying in vacuum, but only moderate temperatures were employed to guard against heat degradation.

All irradiations were performed in the Battelle Gamma Facility. The pool housing the Co⁶⁰ source is 6 by 8 by 14 ft deep. The geometry of the source as used in these experiments yields a dose rate of about 2×10^5 rep per hr, as measured with a CO₂-graphite ion chamber. The ion chamber was calibrated with a chemical dosimeter.

Purification of Monomers

Methyl methacrylate (MMA) from Rohm and Haas was washed with three equal volumes of an aqueous solution containing 5 per cent NaOH and 10 per cent NaCl to remove the hydroquinone inhibitor. This was followed by three washes with deionized water to reduce the ionic residue. The third wash water was neutral to pH paper. The monomer was then dried over anhydrous CaSO₄ for a minimum of 24 hr followed by an equal drying period over CaH₂.

The distillation was carried out under vacuum in the presence of CaH₂ in glass apparatus which had been cleaned with chromic acid, flamed under vacuum, and purged with Linde high-purity dry nitrogen. The distilled monomer was kept under nitrogen in cold storage in glass-stoppered bottles.

The other monomers were not washed before distillation. Ethyl vinyl sulfone (EVS), diphenyl allylphosphite (DPAP), and trifluoroethyl vinyl ether (TFEVE) did not contain hydroquinone stabilizer. Similar procedures as for MMA were followed for distillation and storage. TFEVE required only a moderate vacuum for distillation.

Polymerization

All solvents used as polymerization media for radiation or chemically catalyzed systems (except for emulsion polymerizations) were dried either over CaH_2 (toluene, benzene, heptane, hexane, acetonitrile) or silica gel (isopropanol, MEK). They were filtered through sintered glass just prior to use. All glass vessels were either flamed or evacuated at elevated temperature and stored under nitrogen until used.

All polymerization vessels were flushed with dry nitrogen before sealing. Chemically initiated experiments were generally carried out in small Coke bottles or in test tubes equipped with screw caps. Radiation polymerizations were usually performed in Mason jars or test tubes equipped with ground-glass stoppers. In later experiments, these vessels were sealed with wax. Polymerization conditions varied widely in accordance with the type of product desired and will be described in the appropriate sections.

Purification of Polymers

Suspension polymers prepared in heptane were filtered and washed with freshly filtered, dry solvent. Solution polymers were precipitated under high-speed stirring in at least five times their volume of precipitant. After filtering, the product was rinsed with a small quantity of fresh, dry precipitant. The same procedure was used on reprecipitation of polymer solutions.

Emulsions were coagulated with isopropanol or with the following acid-salt solution:

Water	1000 ml
Isopropanol	156 ml
Glacial acetic acid	2 ml
NaCl	104 g
$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	5 g

The coagulated polymer was then filtered and washed with deionized water.

Polymers were dried in a vacuum oven at 60°C generally for 48 hr. Temperatures up to 80°C were used earlier in the program. For the low-molecular-weight PEVS's, evacuation overnight at room temperature was followed by 48 hr at 60°C. The vacuum was broken with dry nitrogen to eliminate atmospheric moisture as much as possible.

Some PMMA resins which were prepared in emulsion were freeze-dried to reduce or eliminate possible water contamination. The polymers were dissolved 20 per cent by weight in benzene. The solutions were coated over the inner surface of Erlenmeyer flasks and frozen in a dry ice-acetone bath. The solvent was sublimed under vacuum, leaving the thoroughly porous polymers. Moderate heating was applied after most of the solvent was evaporated.

Characterization of Polymers

A close approximation of the intrinsic viscosity of polymers was obtained on Cannon-Fenske viscometers at 25 C with 0.2 g of polymers per 100 cm³ of chloroform. Since the β -cyanoethyl acrylate polymers (PCEA) were insoluble in chloroform, aceto-nitrile was substituted. The intrinsic viscosity was assumed to be close to the average of the reduced and inherent viscosities:

$$\text{Reduced viscosity} = [(t_1/t_2)-1]/C ,$$

$$\text{Inherent viscosity} = (\ln t_1/t_2)/C ,$$

where

t_1 = flow time of polymer solution, sec

t_2 = flow time of solvent, sec

C = concentration of polymer solution, g per 100 cm³.

The molecular weight could be calculated for PMMA from the following relationship reported⁽¹⁾ by Bischoff and Desreux:

$$[\eta]_{100 \text{ cm}^3 \text{ per g}} = 4.8 \times 10^{-5} M_w^{0.80} \text{ (chloroform, 25 C)} .$$

The polymers obtained from EVS and TFEVE were of sufficiently low molecular weight to make an absolute determination by vapor-pressure osmometry possible. Readings were obtained on four concentrations in acetone with a Mechrolab instrument, and number-average molecular weights were obtained graphically according to the method recommended by the manufacturer.

Electrical Testing

Electrical measurements were made on molded disks 2 in. in diameter. Aluminum foils were positioned on both sides of the disks with a thin film of silicon grease. The thickness of the samples without the foils was determined by averaging 10 readings taken with a micrometer caliper to 10^{-4} in. Samples were kept in a desiccator over CaSO₄, and readings were obtained at 72 to 76 F on a General Radio Corporation Type No. 716-C Schering bridge and a Type No. 1690-A sample holder. Considerable interference at the 0.1-kc frequency reduced the reliability of these measurements. The interference was much weaker at 1 kc and hardly noticeable at 10 kc and 100 kc.

The dielectric constant K and the dissipation factor D were calculated as follows:

$$K = \frac{C_p}{C_v} ,$$

$$D = \frac{(D_1 - D_2)(C_2 + C_o)}{C_p} ,$$

(1) References at end.

where

$$C_v = \frac{0.1766 d^2}{t}$$

$$C_p = C_2 - C_1 + C_v$$

$$C_o = C_v + 13$$

C_1 = capacitance reading of sample, $\mu\mu f$

C_2 = capacitance reading of an equal volume of air, $\mu\mu f$

D_1 = dissipation factor of sample

D_2 = dissipation factor of an equal volume of air

d = diameter of sample, in.

t = thickness of sample, in.

Methyl Methacrylate

MMA was used to explore the effects of different polymerization and purification techniques and of sample-preparation and testing methods. It is a common monomer of relatively high dielectric constant which lends itself readily to all types of polymerization.

Preparation of Oxygen-Free Polymers

According to a paper by E. B. Fitzgerald and P. F. Stehle⁽²⁾, lacquers prepared from oxygen-free PMMA had considerably better gloss retention and lower weight loss on exposure to ultraviolet light than lacquers prepared from conventional PMMA. The improvement was attributed to the absence of UV-absorbing carbonyl groups. A brief evaluation of the meaning of this observation to dielectric properties was undertaken early in the program.

Dry monomer and dry toluene were separately distilled from Wood's metal under nitrogen just above the melting point of the alloy, between 70 and 75 C. The reagents and a small amount of AIBN were combined in a dry-nitrogen atmosphere in vacuum-dried Coke bottles.

Polymerization in the presence of Wood's metal gave rise to a fine dispersion of metal oxide which could not be separated by filtration under pressure. Clean polymers from the above reagents were obtained in the absence of Wood's metal. UV spectra of these polymers in the range of 2800 to 3400 Å showed lower absorption than conventional polymers, but not as low as the reference spectrum published by Fitzgerald and Stehle. A spectrum similar to that obtained by Fitzgerald and Stehle was obtained from MMA and toluene distilled from Wood's metal directly into the reaction vessel and sealed under nitrogen before polymerization in the Co^{60} source.

On the basis of these experiments, it was believed that small amounts of oxygen must apparently be responsible for relatively large changes in the UV spectrum. It appeared unlikely that bulk properties like the dielectric constant and dissipation factor could be materially affected in a polar polymer by small oxygen contamination, and work with oxygen-free PMMA was discontinued.

Polymerization

Solution Polymers. PMMA was prepared in toluene solution with the aid of 0.1-0.5 w/o azodiisobutyronitrile (AIBN) or benzoyl peroxide as outlined in Table 1. The reactions were carried out under nitrogen in acid-cleaned Coke bottles with end-over-end agitation. The higher catalyst concentrations gave rise to higher yields and lower molecular weights. A fourfold increase in the polymerization time (Runs 34-16 and 34-17) resulted in a somewhat increased yield and slightly lower molecular weight. At comparable catalyst concentration, benzoyl peroxide produced somewhat lower yields and molecular weights than AIBN.

Emulsion Polymers. Several polymers were prepared by the emulsion recipes summarized in Table 1. The procedure was similar to that used for the solution polymers. In some of the formulations t-dodecyl mercaptan was used to reduce the high molecular weights obtained by this method. In Runs 50-19 and 50-20, the reaction was carried out at 75 C in an attempt to reduce the molecular weights still further. Yields in excess of 100 per cent of theoretical probably indicate the presence of emulsifier and salts in the coagulated polymer. As would be expected, the yields are slightly lower in the isopropanol-coagulated polymers.

Radiation Polymers. Both suspension polymers (in heptane) and solution polymers (in benzene) were prepared in the Co^{60} source (see Table 2). Under similar reaction conditions, the suspension polymers exhibited higher yields and higher molecular weights. Both of these parameters were also strongly affected by the monomer concentration.

Dielectric Properties

Reproducibility of Data. An examination of the reproducibility of dielectric data on different samples of two commercial resins disclosed an unexpected variation with thickness (see Table 3). While the data on two different samples of similar thickness were quite comparable in both resins, a third sample at approximately half the thickness gave from 3 to 5 per cent lower values for K and from 5 to 11 per cent lower values for D (a 23 per cent lower value for D at 100 cycles should be discounted because of the unreliability of the measurements at this frequency).

This observation was substantiated for four molded disks of an AIBN-catalyzed polymer (34-16) and a benzoyl peroxide-catalyzed polymer (34-17) as shown in Table 4. Two of the disks of approximately equal thickness gave very similar results, while a sample of about twice the thickness had higher values, and a sample of about half the

TABLE 1. CHEMICALLY CATALYZED^(a) PMMA

	<u>Azobisisobutyronitrile</u>			
	<u>AIBN-Catalyzed Solution Polymers</u>		<u>Benzoyl Peroxide-Catalyzed Solution Polymers</u>	
	<u>6-1</u>	<u>6-2</u>	<u>6-3</u>	<u>34-16</u>
Monomer, volume per cent	40	40	40	40
Solvent	Toluene	Toluene	Toluene	Toluene
Catalyst Based on Monomer, w/o	0.1	0.2	0.5	0.1
Reaction Time, hr	6	6	6	24
Reaction Temperature, C	75	75	75	75
Precipitant	Heptane	Heptane	Heptane	Heptane
Yield, per cent	58.0	74.5	91.8	77.0
Molecular Weight ^(b)	240,000	140,000	73,000	227,000
	<u>Emulsion Polymers</u>			
	<u>14-10</u>	<u>14-11</u>	<u>17-12</u>	<u>17-13</u>
Monomer, volume per cent	30	30	30	30
Emulsifier, Based on Monomer, w/o	5	5	8	8
K ₂ S ₂ O ₈ Based on Monomer, w/o	0.2	0.2	0.2	0.2
Na ₂ S ₂ O ₅ Based on Monomer, w/o	0.4	0.4	0.4	--
t-Dodecyl mercaptan Based on Monomer, w/o	--	0.2	--	--
Reaction Time, hr	24	24	8	4
Reaction Temperature, C	30	30	30	75
Precipitant	Isopropanol		Acid-salt solution ^(c)	Acid-salt solution ^(c)
Yield, per cent	100.4	97.3	103	109.5
Molecular Weight ^(b)	3,100,000	983,000	2,864,000	685,000
				103.8
				487,000

(a) Polymerized in Coke bottles with end-over-end agitation.

(b) Calculated from viscosity relationship.

(c) See section "Laboratory and Testing Procedure" for more detailed description.

TABLE 2. RADIATION^(a)-CATALYZED PMMA

	<u>20-14</u>	<u>61-22</u>	<u>61-21.1</u>	<u>61-23</u>	<u>61-24</u>
Monomer, volume per cent	25	30	25	20	15
Solvent	Heptane	Heptane	Heptane	Heptane	Heptane
Reaction Time, hr	6	2	4	8	16
Dose Rate, 10^5 rep per hr	2	2	2	2	2
Total Dose, 10^5 rep	12	4	8	16	32
Yield, per cent	58.8	8	100	78	90
Molecular Weight ^(b)	96,700	394,000	500,000	127,000	70,000
	<u>62-25</u>	<u>62-26</u>	<u>83-27</u>	<u>83-28</u>	<u>21-15</u>
Monomer, volume per cent	25	30	30	18	25
Solvent	Benzene ^(c)	Benzene ^(c)	Benzene ^(c)	Heptane	Heptane
Reaction Time, hr	4	2	8	16	1
Dose Rate, 10^5 rep per hr	2	2	1.7	1.7	5.8
Total Dose, 10^5 rep	8	4	13.6	27.2	5.8
Yield, per cent	9	4.8	50.1	27.6	12.8
Molecular Weight ^(b)	89,000	114,000	98,500	82,800	70,700

(a) In Co⁶⁰ source.

(b) Calculated from viscosity relationship.

(c) Precipitated in hexane.

TABLE 3. REPRODUCIBILITY OF DIELECTRIC DATA OF TWO COMMERCIAL POLYMERS^(a)

	Plexiglas V			Plexiglas VS		
	1	2	3	1	2	3
Average Sample Thickness, in.	<u>0.0980</u>	<u>0.0974</u>	<u>0.0504</u>	<u>0.0983</u>	<u>0.0978</u>	<u>0.0492</u>
Dielectric Constant (K)						
0.1 Kc	3.24	3.29	3.15	3.40	3.37	3.23
1 Kc	3.00	3.04	2.93	3.14	3.13	3.01
10 Kc	2.85	2.88	2.78	2.97	2.97	2.87
100 Kc	2.75	2.77	2.68	2.84	2.84	2.75
Dissipation Factor (D)						
0.1 Kc	0.0613	0.0659	0.0558	0.0700	0.0600	0.0511
1 Kc	0.0419	0.0436	0.0406	0.0440	0.0426	0.0386
10 Kc	0.0302	0.0313	0.0293	0.0322	0.0325	0.0300
100 Kc	0.0233	0.0242	0.0223	0.0264	0.0267	0.0244

(a) Samples were molded for 30 min at 300 F.

TABLE 4. THE EFFECT OF SAMPLE THICKNESS AND MOLDING CONDITIONS ON THE DIELECTRIC PROPERTIES OF PMMA

34-16						
Molding Temperature, F	300	300	300	300	400	400
Molding Time, min	30	30	30	30	30	30
Average Sample Thickness, in.	.0924	.0481	.0484	.0287	.0987	.0476
Dielectric Constant (K)						
0.1 Kc	3.20	2.98	2.99	2.93	3.42	3.65
1 Kc	2.96	2.80	2.78	2.73	3.16	3.43
10 Kc	2.80	2.64	2.63	2.59	2.99	3.29
100 Kc	2.69	2.55	2.54	2.50	2.87	3.20
Dissipation Factor (D)						
0.1 Kc	.0612	.0552	.0569	.0499	.0600	.0450
1 Kc	.0458	.0405	.0417	.0374	.0447	.0332
10 Kc	.0318	.0284	.0291	.0263	.0310	.0234
100 Kc	.0288	.0201	.0202	.0195	.0236	.0173
34-17						
Molding Temperature, F	300	300	300	300	400	400
Molding Time, min	30	30	30	30	30	30
Average Sample Thickness, in.	.0925	.0559	.0568	.0287	.0911	.0488
Dielectric Constant (K)						
0.1 Kc	3.20	3.02	3.07	2.75	3.43	3.23
1 Kc	2.94	2.81	2.85	2.57	3.15	2.95
10 Kc	2.79	2.67	2.71	2.45	2.98	2.79
100 Kc	2.68	2.57	2.61	2.37	2.87	2.70
Dissipation Factor (D)						
0.1 Kc	.0569	.0543	.0545	.0478	.0622	.0709
1 Kc	.0444	.0402	.0398	.0355	.0461	.0461
10 Kc	.0313	.0284	.0289	.0251	.0307	.0295
100 Kc	.0233	.0206	.0217	.0178	.0221	.0203

TABLE 5. DIELECTRIC DATA FOR

	6-1	6-2	6-3	6-1	6-2	6-3	Repre-
				First Measurement			
Yield, per cent of theoretical	58.0	74.5	91.8	--	--	--	
Molecular Weight ^(b)	240,000	140,000	73,000	--	--	--	
Molding Temperature, F	275	275	275	275	275	275	
Molding Time, min	15	15	15	15	15	15	
Average Sample Thickness, in.	0.0492	0.0489	0.0493	0.0553	0.0528	0.0560	
Dielectric Constant (K)							
0.1 Kc	2.92	2.91	2.85	2.96	2.96	3.07	
1 Kc	2.72	2.71	2.85	2.77	2.75	2.86	
10 Kc	2.60	2.58	2.53	2.64	2.62	2.73	
100 Kc	2.51	2.50	2.45	2.56	2.54	2.64	
Dissipation Factor (D)							
0.1 Kc	0.0535	0.0546	0.0478	0.0509	0.0567	0.0543	
1 Kc	0.0382	0.0383	0.0393	0.0376	0.0397	0.0398	
10 Kc	0.0265	0.0263	0.0261	0.0265	0.0271	0.0270	
100 Kc	0.0188	0.0180	0.0178	0.0195	0.0190	0.0191	
	10-6	10-7	10-8	10-7	10-8	34-17	Repre-
							cipitated
Yield, per cent of theoretical	43.8	57.5	82.0	--	--	74.3	--
Molecular Weight ^(b)	320,000	213,000	127,000	--	--	290,000	--
Molding Temperature, F	275	275	275	300	300	300	300
Molding Time, min	15	15	15	30	30	30	30
Average Sample Thickness, in.	0.0493	0.0492	0.0485	0.0477	0.0410	0.0547	0.0482
Dielectric Constant (K)							
0.1 Kc	2.94	3.03	3.01	3.07	2.90	3.01	2.93
1 Kc	2.73	2.79	2.77	2.84	2.70	2.78	2.72
10 Kc	2.59	2.64	2.62	2.70	2.57	2.64	2.60
100 Kc	2.51	2.55	2.53	2.61	2.49	2.55	2.51
Dissipation Factor (D)							
0.1 Kc	0.0595	0.0649	0.0697	0.0592	0.0546	0.0635	0.0552
1 Kc	0.0419	0.0445	0.0455	0.0412	0.0380	0.0426	0.0396
10 Kc	0.0273	0.0287	0.0294	0.0274	0.0256	0.0282	0.0282
100 Kc	0.0176	0.0184	0.0187	0.0182	0.0174	0.0181	0.0211

(a) These samples were rerun 1 day after the first determination to evaluate the reproducibility of readings.

(b) Viscosity molecular weights were calculated according to Bischoff and Desreux, J. Polymer Sci., 10, 437 (1953).

CHEMICALLY CATALYZED PMMA

cipitated			Reprecipitated			Reprecipitated		
Second Measurement(a)			Reprecipitated					
6-1	6-2	6-3	6-1	6-2	6-3	34-16		34-16
--	--	--	--	--	--	77		--
--	--	--	--	--	--	227,000		--
275	275	275	400	400	400	300		300
15	15	15	15	15	15	30		30
0.0553	0.0528	0.0560	0.0486	0.0508	0.0516	0.0522		0.0465
2.96	2.99	3.11	2.71	3.13	3.39	3.02		2.79
2.77	2.75	2.86	2.60	2.90	3.12	2.78		2.60
2.64	2.62	2.73	2.41	2.76	2.98	2.64		2.48
2.55	2.54	2.64	2.34	2.66	2.88	2.55		2.40
0.0512	0.0623	0.0636	0.0596	0.0592	0.0664	0.0606		0.0510
0.0375	0.0415	0.0411	0.0372	0.0415	0.0467	0.0429		0.0380
0.0264	0.0271	0.0271	0.0249	0.0277	0.0307	0.0281		0.0273
0.0194	0.0190	0.0194	0.0173	0.0188	0.0204	0.0188		0.0201
Filtered and Re- cipitated								
14-10	14-11	17-12	17-13	17-13	14-11	17-13	50-19	50-20
100.4	97.3	103	109.5	--	--	--	103.8	107
3,100,000	983,000	2,864,000	684,000	--	--	--	1,862,000	487,000
300	300	300	300	300	300	300	300	300
30	30	30	30	30	30	30	30	30
0.0488	0.0488	0.0526	0.0511	0.0391	0.0469	0.0476	0.0482	0.0510
2.92	2.95	3.16	3.13	3.12	2.74	2.86	3.88	3.21
2.72	2.75	2.94	2.89	2.90	2.56	2.65	3.57	2.95
2.60	2.63	2.80	2.75	2.76	2.45	2.54	3.39	2.79
2.51	2.54	2.70	2.65	2.66	2.38	2.46	3.27	2.69
0.0522	0.0536	0.0568	0.0618	0.0390	0.0567	0.0632	0.0637	0.0664
0.0383	0.0382	0.0394	0.0413	0.0371	0.0365	0.0383	0.0422	0.0445
0.0271	0.0272	0.0275	0.0281	0.0283	0.0237	0.0253	0.0282	0.0312
0.0190	0.0195	0.0196	0.0198	0.0222	0.0169	0.0177	0.0199	0.0229

thickness had lower values for K and D. This effect, however, becomes only significant at large variations of thickness, and can be ignored when samples of similar thickness are compared.

Dielectric constants of four samples molded at 400 F showed a definite increase over comparable samples molded at 300 F. The dissipation factors were also influenced by the molding temperature, but differently in the AIBN and in the benzoyl peroxide-initiated polymers.

A comparison between sample disks molded at different temperatures is also available from the data in Table 5. The reproducibility of two readings on consecutive days on reprecipitated polymers from Runs 6-1, 6-2, and 6-3 was excellent. Samples of these resins molded at a higher temperature, however, exhibited considerable changes in dielectric data. It appears that increases and decreases in the dielectric data due to higher molding temperatures are dependent on the catalyst concentration used for the polymerization. Another comparison can be made between moldings made at different temperatures of benzoyl peroxide-initiated polymers from Runs 10-7 and 10-8, with results which differ again from those of the AIBN-prepared PMMA's.

For the present program, only samples prepared under comparable molding conditions could be compared with one another.

Discussion of Results. The effect of AIBN concentration on the dielectric properties of the polymers should be evident from the comparison of the data for Runs 6-1, 6-2, and 6-3 in Table 5 and the effect of the benzoyl peroxide concentration from Runs 10-6, 10-7, and 10-8. No convincing pattern can be found in the first series in either K or D. In the second series the values for K appear again unchanged, while the D values show a consistent, though small, increase with catalyst concentration. The comparisons are complicated by the molecular-weight differences in these polymers, the maximum being a threefold difference. Comparison of 14-10 with 14-11 which also shows a threefold difference in molecular weight, leads, however, to the conclusion that molecular weight plays no important role. There is also a tendency for the benzoyl peroxide-initiated polymers to exhibit somewhat higher dielectric properties than the corresponding AIBN-initiated resins. This is not borne out in all cases, however (see 34-16 and 34-17).

The re-evaluation of the electrical properties of polymers from Runs 6-1, 6-2, and 6-3 after reprecipitation resulted in a small, but unexpected increase in some of these properties. In similar experiments with 34-16 and 34-17 polymers, however, the expected reduction in the K and D values was usually realized.

Emulsion polymers coagulated with isopropanol (14-10 and 14-11) had dielectric properties which were similar to those of the solution polymers. On the other hand, coagulation with an acid-salt solution gave polymers with markedly increased values for K and D (17-12, 17-13, 50-19, and 50-20). Two of the emulsion polymers were freeze-dried to facilitate the complete removal of volatiles. The electrical data for these resins were greatly reduced, falling even below those of most of the solution polymers. This would indicate that the latter may still contain some volatiles, even after prolonged drying in a vacuum oven.

Some commercially available PMMA's were subjected to electrical testing, and the results are summarized in Table 6. Both K and D measurements were higher than those of most laboratory preparations, indicating the presence of considerable amounts of impurities, with unreacted monomer the most likely suspect. The molded specimens were stored over CaSO_4 in a desiccator prior to testing, which accounts for the differences between these data and those reported at 50 per cent relative humidity by the manufacturer.

TABLE 6. DIELECTRIC DATA FOR SOME COMMERCIAL PMMA RESINS

	Lucite ^(a) 2008	Lucite ^(a) 2010	Lucite ^(a) 2041	Plexiglas ^(b) V	Plexiglas ^(b) VS
Molecular Weight ^(c)	23,000	80,000	375,000	78,000	87,000
Molding Temperature, F	275	275	275	300	300
Molding Time, min	15	15	15	30	30
Average Sample Thickness, in.	.0699	.0630	.0614	.0504	.0492
Dielectric Constant (K)					
0.1 Kc	3.13	3.09	3.08	3.15	3.23
1 Kc	2.88	2.86	2.86	2.93	3.01
10 Kc	2.74	2.72	2.72	2.78	2.87
100 Kc	2.64	2.62	2.63	2.68	2.75
Dissipation Factor (D)					
0.1 Kc	.0691	.0650	.0614	.0558	.0511
1 Kc	.0423	.0416	.0409	.0406	.0386
10 Kc	.0288	.0295	.0276	.0293	.0300
100 Kc	.0211	.0216	.0203	.0223	.0244

(a) Trademark for Du Pont polymethyl methacrylate resins.

(b) Trademark for Rohm and Haas polymethyl methacrylate resin.

(c) Viscosity molecular weights were calculated according to Bischoff and Desreux, J. Polymer Sci., 10, 437 (1953).

In Table 7, the results of the electrical testing of the radiation polymers are presented. The data for the solution polymers appear to be similar to those for the suspension polymers of parallel molding history. There is little variation in the data, indicating that the effects of monomer concentration and irradiation dose must be small, if present.

Some representative compositions from each type of polymerization system molded under comparable conditions were selected for comparison in Table 8. At about the same dielectric constants, there is very little difference in the dissipation factors of the various resins. The radiation polymers may have a slight advantage at the lower frequencies which are of particular importance for electroluminescent applications. However, the differences are too small to be of any practical importance.

TABLE 7. SUMMARY OF DIELECTRIC DATA FOR PMMA PREPARED BY RADIATION

	<u>61-21.1</u>	<u>61-22</u>	<u>61-23</u>	<u>61-24</u>	<u>62-25</u>	<u>62-26</u>
Solvent	Heptane	Heptane	Heptane	Heptane	Heptane	Heptane
Monomer Concentration, volume per cent	25	30	20	15	25	30
Irradiation Time, hr	4	2	8	16	4	2
Total Dose, 10^5 rep	8	4	16	32	8	4
Yield, per cent of theoretical	>100	8.0	78	90	9.0	4.75
Viscosity Average Molecular Weight	557,000	394,000	127,000	70,000	89,000	114,000
Molding Temperature, F	300	300	300	300	300	300
Molding Time, min	15	30	15	15	30	15
Average Thickness, in.	.0518	.0465	.0459	.0542	.0515	.0476
Dielectric Constant (K)						
0.1 Kc	3.16	3.05	3.11	3.17	3.22	2.99
1 Kc	2.94	2.81	2.88	2.95	2.97	2.79
10 Kc	2.78	2.67	2.74	2.80	2.82	2.65
100 Kc	2.68	2.57	2.63	2.69	2.71	2.56
3.06						
Dissipation Factor (D)						
0.1 Kc	.0553	.0548	.0559	.0556	.0600	.0543
1 Kc	.0411	.0416	.0418	.0415	.0418	.0394
10 Kc	.0295	.0281	.0299	.0292	.0296	.0282
100 Kc	.0216	.0207	.0224	.0215	.0227	.0215
.0551						

TABLE 8. COMPARISON OF DIELECTRIC DATA FOR PMMA PREPARED BY RADIATION AND BY CHEMICAL CATALYSIS

	<u>61-21.1</u>	<u>61-24</u>	<u>17-13</u>	<u>34-16</u>	<u>34-17</u>
Polymerization System	Suspension	Suspension	Emulsion	Solution	Solution
Catalyst	Radiation	Radiation	Potassium persulfate	AIBN	Benzoyl peroxide
Yield, per cent of theoretical	>100	90	>100	77	74
Viscosity Average Molecular Weight	557,000	70,000	684,000	230,000	288,000
Molding Temperature, F	300	300	300	300	300
Molding Time, min	30	30	30	30	30
Average Sample Thickness, in.	.0465	.0426	.0511	.0522	.0547
Dielectric Constant (K)					
0.1 Kc	3.05	3.06	3.13	3.02	3.01
1 Kc	2.81	2.83	2.89	2.78	2.78
10 Kc	2.67	2.69	2.75	2.64	2.64
100 Kc	2.57	2.59	2.65	2.55	2.55
Dissipation Factor (D)					
0.1 Kc	.0548	.0551	.0618	.0606	.0635
1 Kc	.0416	.0402	.0413	.0429	.0426
10 Kc	.0281	.0282	.0281	.0281	.0282
100 Kc	.0207	.0211	.0198	.0188	.0181

Conclusions. From the results of this work it was concluded that:

- (1) Radiation-induced PMMA has little, if any, advantage over the best chemically initiated polymers. The low catalyst level required to polymerize MMA does not contribute substantially to dielectric loss, while volatile residues such as solvents and monomers contribute to the lossiness of all polymers alike.
- (2) Varying radiation doses from 4 to 32×10^5 rep have no marked effect on the electrical properties of the products.
- (3) Reproducibility of dielectric measurements on the same specimen and on different specimen of similar thickness of the same polymer is quite good (usually better than 1 per cent at the higher frequencies and always better than 2 per cent for K; between 1 and 4 per cent at 1 to 100 kc, but usually much poorer at 0.1 kc for D).
- (4) The molding conditions have a very pronounced effect on the dielectric properties of PMMA. The effect in different polymers has not been uniform, however, and remains unpredictable.
- (5) No noticeable effect on dielectric properties has been observed in the weight-average molecular-weight range from 70,000 to 3,000,000.
- (6) AIBN-initiated PMMA's usually have slightly lower dielectric data than comparable benzoyl peroxide-initiated materials. The effect is quite small, however, and has not been unequivocally established.
- (7) Emulsion polymers coagulated with isopropanol have dielectric properties similar to solution polymers, but those coagulated with a standard acid-salt solution have much higher K and D values.
- (8) Freeze-drying lowers the electrical measurements of emulsion polymers below the values of many solution polymers. It appears, therefore, that the high values obtained from emulsion polymers are largely due to volatiles and that solution polymers may also contain some volatile residues.

β -Cyanoethyl Acrylate

This monomer was selected because it contains one of the strongest polar groups, the nitrile group, five atoms removed from the backbone of the polymerized structure. This long pendant chain bestows great mobility on the dipole, enabling it to orient in the electric field. It is, moreover, responsible for the low glass transition temperature which permits greater molecular motion at room temperature. PCEA may, therefore, be expected to exhibit higher dielectric constants than any of the other commercially available monomers in common use.

Polymerization

β -CEA from Union Carbide Corporation was dried and distilled from CaH_2 . Bottle polymerizations were undertaken in benzene with 10 and 20 volume per cent monomer concentrations and 0.5 and 1.0 w/o free-radical catalysts such as AIBN and benzoyl peroxide (see Table 9). Polymer collected around the sides of the bottles, while no additional precipitate was obtained on mixing with isopropanol, indicating that no soluble fraction remained in the benzene. The deposit of solid product on the bottles is undesirable because of the difficulty of freeing the polymers from absorbed monomer and solvent without reprecipitation. Additional reactions were, therefore, undertaken in other media.

Good yields were achieved in MEK with fairly low catalyst concentrations and short reaction times. Methyl chloroform was substituted for isopropanol as a precipitant in later experiments because it is less susceptible to moisture absorption and because of its somewhat lower boiling point.

PCEA preparations in MEK were cloudy, indicating borderline solubility, but clear solutions were obtained in acetonitrile. Polymers prepared in the latter solvent had higher molecular weights than similar preparations in MEK. Lower CEA concentrations were employed in an effort to prevent gelling due to reaction at the α -hydrogen. At 0.2 w/o AIBN and 10 volume per cent monomer concentration no yield was obtained, and a repetition of the experiment verified this result. A similar reaction with 20 volume per cent monomer concentration had given a high yield of gelled product. The monomer concentration is apparently very critical.

Benzene was also quickly abandoned as a medium for radiation polymerization when gelled polymers were obtained even at very low doses (see Table 10). An attempt to limit crosslinking by reducing the CEA concentration to 2 and 3 volume per cent was unsuccessful, since no polymer formed at the low dose rates used. As in the work with chemical catalysts, cloudy solutions were formed in MEK and clear solutions in acetonitrile. The latter solvent also led to products having a molecular weight higher than the former.

Dielectric Properties

Two-inch disks were molded at 225 F and 15 min. In spite of these mild molding conditions, numerous bubbles formed in the samples and also created uneven surfaces. Although stringent drying conditions were observed with these as with all polymers, it appears likely that a small residue of polar solvent remained in the resins. This hypothesis gained support when it was established that polymers prepared in acetonitrile had consistently higher K and D readings than similar ones prepared in MEK. The higher boiling point and greater polar affinity of acetonitrile makes it more difficult to remove this solvent than MEK.

The imperfections of the molded specimen rendered the accurate determination of dielectric data impossible. Using three methods to determine thickness of the soft, uneven samples (with a micrometer, an Ames gage, and the sample holder), three different sets of values for K and D were obtained on each sample. With maximum variations of 10 to 20 per cent in the K and D values of any one sample, there was no hope of distinguishing the effect of the various polymerization catalysts. It could be established, however, that the K readings were quite high (between 12 and 18 at the

TABLE 9. CHEMICALLY CATALYZED POLY(β -CYANOETHYL ACRYLATE)

	<u>84-151</u>	<u>84-153</u>	<u>84-152</u>	<u>84-154</u>	<u>87-158</u>	<u>87-157</u>	<u>113-170</u>	<u>113-169</u>	<u>102-167</u>	<u>102-166</u>	<u>113-172</u>	<u>113-171</u>
Solvent	Benzene	Benzene	Benzene	Benzene	MEK	MEK	MEK	MEK	Acetonitrile	Acetonitrile	Acetonitrile	Acetonitrile
Monomer, volume per cent	20	20	10	20	20	20	10	10	20	20	10	10
AIBN Based on Monomer, w/o	1.0	0.5	0.5	--	0.5	0.2	0.5	0.2	0.5	0.2	0.5	0.2
Benzoyl Peroxide Based on Monomer, w/o	--	--	--	0.5	--	--	--	--	--	--	--	--
Reaction Time, hr	8	48	72	48	6-1/4	6-1/4	6	6	7	7	6	6
Reaction Temperature, C	60	60	60	60	60	60	60	60	60	60	60	60
Precipitant	Isopro- panol	Isopro- panol	Isopro- panol	Isopro- panol	Isopro- panol	Methyl chloroform						
Yield, per cent	--	--	--	--	94.8	60.8	61.0	25.3	92.5	Gel	60.6	None
$[\eta]$ in Acetonitrile	--	--	--	--	0.286	0.322	0.204	--	1.17	--	0.386	--

TABLE 10. RADIATION-CATALYZED POLY(β -CYANOETHYL ACRYLATE)

lower frequencies and between 9 and 14 at the higher frequencies) and that the D readings lay mostly between 0.03 and 0.06 and went through a minimum at 10 kc in every sample tested.

Ethyl Vinyl Sulfone

This monomer was selected for investigation because it contains one of the strongest polar groups. The structurally similar dimethylsulfone(3) and diethylsulfone(4) have dipole moments of 4.41, while the strongly polar nitrile group is responsible for dipole moments of 3.56 and 3.51 in propionitrile(5) and acrylonitrile(6), respectively. Other dipole moments of comparable organic substances reported in the literature include acetamide(7), 3.72; nitroethane(8), 3.19; acetaldehyde(9), 2.49; acrolein(9), 2.88; 1,1,1-trifluoroethane(10), 2.37; ethyl chloride(11), 1.8; vinyl chloride(12), 1.44; ethyl alcohol(13), 1.66; ethylamine(5), 1.37; and dimethyl ether(14), 1.28. On this basis, a high dielectric constant could be anticipated in the polymer, provided the sulfone group was not deprived of its mobility due to its proximity to the backbone of the chains.

Polymerization

Inhibitor-free EVS, as received from Monomer-Polymer Laboratories, was reacted at 60 C as a 20 per cent solution by volume in benzene with 0.2 w/o AIBN based on the monomer (see Table 11). After 69 hr agitation, the yield was negligible. AIBN concentrations of 0.5 and 1.0 w/o in the same system produced 28 and 40 per cent yields, respectively. By increasing the EVS concentration to 30 volume per cent, the yield was raised to 54 per cent. Substituting benzoyl peroxide for AIBN resulted in poorer conversion, even when the temperature was raised to 85 C.

Experiments were also conducted in polar solvents such as MEK and acetonitrile in an effort to raise the yield. These attempts, however, were unsuccessful, and 50 to 55 per cent conversion was the maximum obtainable at 30 volume per cent monomer concentration and 1 w/o AIBN concentration.

The polymerization experiments summarized in Table 12 illustrate the same resistance to polymerization in the Co⁶⁰ source as had already been demonstrated with chemical free-radical catalysts. The monomer concentration in benzene had to be raised to 30 volume per cent and a fairly high dose of 6.5×10^6 rep had to be employed before 48 per cent conversion was achieved (94-115). Further increases in the dose up to 1.1×10^7 rep had only a small effect on the yield (100-117). Irradiation at 60 C to 7.68×10^6 rep (158-124) was also ineffective, and an experiment at a higher dose rate to 2.45×10^7 rep brought the yield only up to 62 per cent (159-125).

A gas-liquid chromatographic analysis was performed on EVS to search for a possible cause of the poor conversion results in all types of recipes. The purity of the monomer as received was established at 98.6 per cent. Almost all the impurities, or 1.3 per cent, were concentrated in a peak close to and slightly above the monomer peak. It is believed that this may be diethylsulfone, which would not be expected to interfere with the polymerization. A vacuum distillation from CaH₂ did not improve the purity of the monomer. However, all later polymerization experiments starting with Run 94-114 were conducted with distilled EVS.

TABLE II. CHEMICALLY CATALYZED POLY(ETHYL VINYL SULFONE)

	<u>66-101</u>	<u>81-103</u>	<u>85-106</u>	<u>104-118(a)</u>	<u>108-119</u>	<u>66-102</u>	<u>109-120</u>	<u>109-121</u>	<u>81-104</u>	<u>85-107</u>	<u>115-123</u>	<u>115-122</u>	<u>81-105</u>
Solvent	Benzene	Benzene	Benzene	Benzene	Benzene	MEK	Acetonitrile	Benzene	Benzene	Benzene	Benzene	Benzene	MEK
Monomer, volume per cent	20	20	20	30	20	30	30	20	20	20	30	30	20
AIBN Based on Monomer, w/o	0.2	0.5	1.0	1.0	0.2	1.0	1.0	1.0	--	--	--	--	--
Benzoyl Peroxide Based on Monomer, w/o	--	--	--	--	--	--	--	--	0.2	1.0	0.2	1.0	0.2
Reaction Time, hr	69	42	46	48	69	48	48	42	46	48	48	48	42
Reaction Temperature, C	60	60	60	60	60	60	60	60	60	60	85	85	60
Yield, per cent	Negligible	28.1	41.2	38.3	53.7	Negligible	27.0	18.0	Negligible	8.8	Negligible	33.3	Negligible
$[\eta]$ in Chloroform(b)	--	0.017	0.024	0.008	0.036	--	0.066	0.038	--	0.062	--	0.019	--
Molecular Weight(c)	--	--	--	740	1100	--	--	--	--	--	930	--	--

(a) This experiment is a scale-up to larger quantities of 85-106.

(b) The average of the reduced and the inherent viscosities at 0.2 w/o concentration.

(c) Determined on a vapor-phase osmometer.

TABLE 12. RADIATION CATALYZED POLY(ETHYL VINYL SULFONE)

	<u>91-108</u>	<u>91-109</u>	<u>93-111(a)</u>	<u>93-110</u>	<u>93-113</u>	<u>93-112</u>	<u>94-114</u>	<u>94-115</u>	<u>100-117</u>	<u>158-124(b)</u>	<u>159-125</u>	<u>99-116(b)</u>
Solvent	Benzene	Benzene	Benzene	Benzene	Benzene	Benzene	Benzene	Benzene	Benzene	Benzene	Benzene	--
Monomer, volume per cent	10	20	20	20	20	30	30	30	30	30	30	100
Reaction Time, hr	4-1/2	4-1/2	4-1/2	8	24	4-1/2	14	38-1/4	64-5/6	48	48	20
Dose Rate, 10^5 rep per hr	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.7	1.7	1.6	1.7
Total Dose, 10^5 rep	5.85	5.85	5.85	10.4	31.2	5.85	18	65	110	76.8	245	34
Yield, per cent	Negligible	2.4	2.2	5.8	18.4	4.2	14.6	48.2	52.0	42.8	62.2	Negligible
$[\eta]$ in Chloroform(c)	--	--	--	--	--	--	0.046	0.053	0.017	--	--	--
Molecular Weight(d)	--	--	--	--	--	--	--	1380	920	--	--	--

(a) This is a rerun of 91-1109 except that extraordinary precautions were used to dry the benzene and the reaction vessel. No improvement in yield was realized.

(b) Experiment 158-124 was run at 60°C and 99-116 in liquid nitrogen at -196°C; all other runs were conducted at pool temperature.

(c) The average of the reduced and the inherent viscosities at 0.2 w/o concentration.

(d) Determined on a vapor-phase osmometer.

A solid-state irradiation of freshly distilled EVS was performed at liquid-nitrogen temperature. At the end of the irradiation, the reaction vessel was kept in a liquid-nitrogen-cooled Dewar and was allowed to come up to temperature slowly. Since no appreciable precipitate was obtained in isopropanol, the liquid was distilled off at high vacuum. A very small quantity of a sticky, yellowish, benzene-insoluble residue remained, which amounted to a very small yield.

In addition to the poor yield realized with this monomer in all types of recipes, the resulting polymer was of very low molecular weight. Consequently, it was possible to determine absolute number-average molecular weights with a vapor-pressure osmometer, and values of 740 to 1380 were obtained. Somewhat higher molecular weights were realized with AIBN in MEK (109-120) and with benzoyl peroxide in benzene (85-107) but they were not sufficiently high to justify the lower yields obtained with these recipes.

Several of the polymerizations were repeated to obtain electrical data on duplicate preparations of the same recipe. The first number of the code, denoting the page in the laboratory book, was changed, but the second number, standing for the recipe was retained, and the third number, signifying the first, second, etc., repetitive preparation was added. Thus, 138-117-1 stands for the first repetition of Recipe 117 on page 138 of the laboratory record book.

Dielectric Properties

With the high catalyst concentrations required to polymerize EVS, it might be expected that the comparison of the dielectric properties would be to the radiation polymers' advantage. The first data collected also appeared to support this expectation. As additional samples of the same polymers were evaluated, however, it became apparent that the results were not reproducible. In several polymers, the dissipation factor appeared to increase with the age of the polymer at the time of molding (see Table 13). There were, however, a few exceptions to this pattern such as the data of Columns 6, 9, and 16 of Table 13.

The aging effect was investigated by redrying polymer from Run 100-117 under vacuum and storing under dry nitrogen in a desiccator to prevent any contact with atmospheric moisture. The test results of the molded specimen are shown in Column 7 of Table 13. A control was molded from the untreated portion, and the data are shown in Column 6. The lower values of the redried polymer suggest that moisture or some volatile product of degradation was removed.

Table 13 also contains the data for the polymer from Run 155-119-2, which was prepared according to the same recipe as used for Runs 108-119 and 138-119-1 but was precipitated in a smaller quantity of isopropanol with less vigorous agitation. The effect of this procedure was to increase both K and D drastically. This experiment illustrates the sensitivity of the dielectric measurements to the precipitation procedure, which determines the impurities left in the resins. While the procedure was kept as constant as possible for the other preparations, there remains the possibility that some of the variations in electrical data stem from this source.

Under these circumstances it became very difficult to evaluate the effect of different catalytic methods. By comparing the first sample of each of the various polymers in Table 13 (before extended aging of the polymer) it must be concluded that the

TABLE 13. SUMMARY OF DIELECTRIC DATA FOR POLY(ETHYL VINYL SULFANE)

Polymerization Catalyst		γ -Radiation from Co_{60}						γ -Radiation from Co_{60}	
		94-115			100-117				
Polymer Identification	94-115								
Column Number	1	$\frac{\alpha(a)}{<10/28}$	$\frac{3}{10/29}$	$\frac{4}{11/27}$	$\frac{5}{12/2}$	$\frac{6}{12/12}$	$\frac{7(b)}{12/11}$		$\frac{8}{12/30}$
Molding Date	<10/28	10/28	10/29	11/30	12/2	12/30	12/30		1/10
Testing Date	10/28	10/28	10/29	11/30	12/2	12/30	12/30		2/21
Sample Thickness, in.	0.0405	0.0423	0.0445	0.0436	0.0434	0.0414	0.0418		0.0428
Dielectric Constant (K)									
0.1 Kc	4.21	4.21	4.80	5.48	4.87	5.12	5.02	5.15	5.11
1 Kc	4.16	4.16	4.72	5.39	4.77	5.04	4.97	5.09	5.06
10 Kc	4.11	4.10	4.64	5.30	4.68	4.97	4.91	5.02	5.00
100 Kc	4.01	4.01	4.50	5.14	4.54	4.83	4.78	4.82	4.84
Dissipation Factor (D)									
0.1 Kc	0.0084	0.0091	0.0152	0.0141	0.0191	0.0117	0.0072	0.0080	0.0059
1 Kc	0.0077	0.0078	0.0109	0.0102	0.0120	0.0089	0.0070	0.0076	0.0060
10 Kc	0.0114	0.0110	0.0137	0.0136	0.0143	0.0124	0.0112	0.0126	0.0101
100 Kc	0.0222	0.0206	0.0261	0.0261	0.0268	0.0244	0.0221	0.0251	0.0208
Polymerization Catalyst									
Polymer Identification	104-118								
Column Number	1.0	$\frac{11}{<10/28}$	$\frac{12}{10/29}$	$\frac{13}{11/29}$	$\frac{14}{12/27}$	$\frac{15}{12/24}$	$\frac{16}{12/31}$	$\frac{17}{11/0}$	$\frac{18(c)}{12/10}$
Molding Date	<10/28	10/29	11/29	12/29	12/27	12/24	12/31	1/22	12/31
Testing Date	11/30	10/29	11/30	12/29	12/29	12/29	12/31	2/21	12/31
Sample Thickness, in.	0.0399	0.0443	0.0407	0.0411	0.0366	0.0394	0.0416	0.0360	0.0410
Dielectric Constant (K)									
0.1 Kc	4.81	5.40	6.73	5.17	5.31	4.50	4.97	7.76	4.58
1 Kc	4.74	5.26	6.14	5.12	5.22	4.41	4.88	7.12	4.55
10 Kc	4.68	5.14	5.83	5.05	5.14	4.33	4.81	6.69	4.51
100 Kc	4.58	4.97	5.55	4.92	5.01	4.23	4.71	6.30	4.42
Dissipation Factor (D)									
0.1 Kc	0.0144	0.0190	0.0818	0.0079	0.0132	0.0152	0.0134	0.0537	0.0054
1 Kc	0.0083	0.0140	0.0398	0.0070	0.0098	0.0111	0.0098	0.0373	0.0052
10 Kc	0.0103	0.0162	0.0286	0.0109	0.0111	0.0124	0.0107	0.0236	0.0113
100 Kc	0.0184	0.0263	0.0353	0.0236	0.0196	0.0213	0.0181	0.0361	0.0179

(a) This sample was molded at 275 F; all others were molded at 225 F.

(b) Redried in vacuum oven and kept under dry nitrogen in a desiccator until molding.

(c) Molded specimen was nearly water-white instead of the yellowish color of most other samples.

dielectric properties of the chemically catalyzed EVS polymers are at least as good as those of the radiation-initiated resins. The dissipation factors of the benzoyl peroxide-catalyzed polymer, Run 115-122, are the lowest of all. The moldings of this resin were almost entirely colorless and transparent, while the moldings of the other polymers tended to be yellowish.

The expectations of high-dielectric constants from PEVS on the basis of the high dipole moment of the sulfone group remained unfulfilled. The molded specimens of these polymers were very hard and brittle. We must conclude, therefore, that the dipole was not fully effective because of lack of mobility, which is in accordance with the discussion published by J. D. Hoffman. (15)

Copolymers of EVS and CEA

The copolymerization of these monomers was undertaken because of the strong polarity of these materials. Since PCEA was soft and flexible at room temperature, CEA was considered as a possible internal plasticizer for the rigid PEVS structure. It was also hoped that higher yields and molecular weights could be achieved with the aid of the readily polymerizable CEA.

Copolymerization

EVS and CEA in the mole ratio of 80:20 were irradiated in benzene (see Run 118-250 in Table 14). The precipitate of the clear liquid in isopropanol was designated as Fraction A and the benzene-insoluble residue at the bottom of the reaction vessel as Fraction B. The latter was dissolved in acetonitrile and precipitated in isopropanol. After drying, both fractions were molded at 225 F and gave clear, dark, reddish-brown samples which were as hard and brittle as the EVS homopolymers, although the nitrogen analysis indicated a CEA content in the resin of 37 mole per cent for Fraction A and 53 mole per cent for Fraction B. In spite of the high irradiation dose and the presence of a large amount of CEA in the product, the total yield of both fractions was only 33.3 per cent, although some improvement over EVS homopolymers was achieved in molecular weight. A similar polymerization in acetonitrile (137-251) produced a polymer material having comparable CEA content and produced about the same or slightly lower yield. The precipitation of the acetonitrile solution into isopropanol gave such a fine suspension that the polymer could not be recovered by filtration and had to be centrifuged. As a result, a small amount of polymer may have been lost, depressing the figure for the yield. Centrifuging is also more likely to leave either solvent or monomer in the resin, which may cause increased K and D measurements.

To learn more about the nature of these copolymers, a blend of the respective homopolymers was prepared by dissolving equal parts in acetonitrile and reprecipitating the clear solution in isopropanol (152-252). A gummy precipitate and a very fine dispersion were obtained which gave the impression of separation of the two constituents. The dispersion was too fine to filter and was discarded. The dried precipitate accounted for only 56.4 per cent of the original weight of the two resins. It was established by nitrogen analysis that the CEA content of the dry polymer was 62 mole per cent, which supports the observation that some PEVS was lost on precipitation. Moldings of this blend were clear and faintly yellow and, surprisingly, as hard and

*ethyl vinyl sulfone
copolymer with acrylate*

TABLE 14. POLYMERIZATION AND DIELECTRIC PROPERTIES OF EVS-CEA COPOLYMERS

Polymer Fraction	118-250		137-251		152-252(a)		152-253(b)	
	A	Benzene	B	Acetonitrile	--	Acetonitrile	--	Acetonitrile
Solvent								
Monomer, volume per cent		30		30		20		30
CEA, monomer mole fraction		0.2		0.2		--		0.5
Reaction Time, hr		49-1/2		49.5		--		48
Dose Rate, 10^5 rep per hr		1.6		1.6		--		1.6
Total Dose, 10^5 rep		79		79		--		76.8
Yield, per cent	13.3		20.0	28.3(c)	56.4		60.0	
CEA in Polymer(d) mole fraction	0.37		0.53	0.50	0.62		0.71	
Molecular Weight(e)	1200		4000	--	--		--	
Sample Thickness(f), in.	0.0288		0.0419	0.0386	0.0442		0.0454	
Dielectric Constant(K)								
0.1 Kc	4.43		6.88	7.61	7.72		12.61	
1 Kc	4.31		6.76	7.21	7.56		11.14	
10 Kc	4.22		6.63	6.96	7.05		10.30	
100 Kc	4.11		6.36	6.66	7.23		9.56	
Dissipation Factor(D)								
0.1 Kc	0.0168		0.0109	0.0246	0.0116		0.0629	
1 Kc	0.0136		0.0101	0.0180	0.0086		0.0428	
10 Kc	0.0140		0.0160	0.0188	0.0128		0.0344	
100 Kc	0.0200		0.0341	0.0320	0.0278		0.0447	

(a) A 50:50 w/o solution of 95-161 (poly-CEA) and 138-117-1 (poly-EVS) in acetonitrile was precipitated in isopropanol like the other polymers.

(b) This was the only pliable resin; all the others were brittle, similar to poly-EVS.

(c) This value may be somewhat low because of the difficulty of recovering the resin.

(d) Corrected for blank run on 138-117-1.

(e) Determined on a vapor-phase osmometer.

(f) Molded at 225 F for 15 min.

brittle as the EVS homopolymers. On the basis of the appearance and the behavior of this polymer blend, it is impossible to judge whether the other compositions are true copolymers or also blends of homopolymers. The insolubility in benzene (such as Fraction B of the polymer from Run 118-250) is strong support, however, for the view that true copolymerization occurred.

Dielectric Properties

The data demonstrate clearly the overwhelming effect of the glass transition temperature (T_g) on the dielectric properties of polymers. Both homopolymers contain a large and comparable concentration of polar groups, with the sulfone of EVS being stronger according to the dipole measurements of model compounds. Yet the homopolymers of CEA which are above their T_g when tested at 72 to 76 F have from three to four times the K-values of the PEVS's which are below their T_g . In copolymers, as large a proportion of CEA as 37 per cent was ineffective in changing the brittleness and hardness of the copolymers. The dielectric readings are correspondingly indistinguishable from those of PEVS. Even with 50 or 60 mole per cent of CEA in the copolymer, the T_g remains below room temperature, although it must be near room temperature, while the K-values are only one and one-half to two times those of PEVS and the D-values are essentially unaffected. At a 70 mole per cent ratio of CEA, the composition is above its T_g at the testing temperature and the K readings are starting to approach those of the still more flexible PCEA. The increase in the D readings is very pronounced (five to six times at the lower frequencies).

Miscellaneous Polymers

Methyl p-Styrenesulfonate

The synthesis of MSS was undertaken according to the directions by Spinner, et al. (16). The monomer appears to be very readily polymerizable, since it reacted on distillation. A small yield of unreacted monomer was obtained and identified by IR.

The polymerized resin was reprecipitated several times from acetone solution, and the resulting product was molded into a hard, clear, deep-reddish-brown specimen 0.0431 in. thick, having the following dielectric properties:

<u>Frequency, kc</u>	<u>K</u>	<u>D</u>
0.1	7.63	0.279
1.0	5.60	0.136
10	4.85	0.067
100	4.40	0.057

The ease of polymerization and unspectacular K-values eliminated this material from further consideration in this program.

β -Trifluoroethyl Vinyl Ether

The conclusion from the first part of this project was that radiation polymerization did not materially improve the dielectric properties of polymers as compared to the results obtained with chemical free-radical catalysts. Attention, therefore, was turned to monomers which are not readily polymerizable by free-radical techniques. β -TFEVE was selected as a commercially available monomer of a type commonly polymerized by ionic initiators. The polymers of β -TFEVE are expected to have high dielectric constants because of the strongly polar CF_3 group, which is sufficiently removed from the polymer chain to be effective.

TFEVE was obtained from Ohio Chemical and Surgical Equipment Company, and was distilled twice from CaH_2 near room temperature under a slight vacuum. Special precautions were taken to flame the apparatus carefully, and the monomer was always distilled directly into the flamed reaction vessels to avoid contact with air because of the well-known sensitivity of ionic polymerizations to moisture.

TFEVE was distilled into a reaction flask containing Hi-Sil 303, and polymerization was allowed to proceed between -50 to -60 C for several hours. The silica was removed by centrifuging a dilute solution in acetone. The polymer was recovered in good yield by precipitation into distilled water (no precipitate formed in methanol or isopropanol). It exhibited cold-flow and was translucent and somewhat tacky. A number-average molecular weight of 20,000 was determined on the vapor-pressure osmometer (Run 103-202).

The polymerization of 103-202 illustrated the adequacy of the purification procedure used with the monomer. Similarly treated TFEVE was irradiated in the Co^{60} source as shown in Table 15. Only low yields of viscous liquids were obtained at low temperatures and low dose rates. At higher dose rates and higher temperatures solid, rubbery polymers were obtained which remained tacky even on thorough vacuum drying. When too high a total dose was administered, the polymer was gelled, but colorless, transparent product could be obtained in good yield when an appropriate irradiation dose was chosen. A much higher dose was required to polymerize TFEVE in benzene solution, and the yield was only about 25 per cent.

A comparison of the dielectric data of Run 103-202 (catalyzed with acidic silica) and Run 161-206 (radiation polymerized) is given in Table 16. A moderate molding temperature of 160 F was sufficient to mold samples, which were quite soft and easily deformable. This was especially pronounced in the polymer from Run 161-206, which was apparently of lower molecular weight. The thickness of the specimens could not be determined as accurately as for the other polymers because the pressure of the gage was sufficient to deform the soft resin and a strong drift was observed in the readings. Consequently, the electrical measurements were correspondingly less accurate.

In spite of these difficulties, reproducibility of the dielectric constants of the two specimens of the polymer from Run 161-206 ranged between 0.6 and 2.7 per cent. The reproducibility of the dissipation factors lay between 1.3 and 5.6 per cent at the three higher frequencies, and only at 0.1 kc was the difference between the two values as high as 11.5 per cent. If, therefore, the D-values of this frequency are eliminated from the comparison of the two resins, the dissipation factors of the radiation polymers are slightly lower than those of the chemically catalyzed resin, while the differences in the K-values fall within the limits of the indicated reproducibility. The advantage of the radiation polymer appears to be too small to be significant.

TABLE 15. RADIATION-CATALYZED POLY (β -TRIFLUOROETHYL VINYL ETHER)

	<u>96-201</u>	<u>103-203</u>	<u>116-204</u>	<u>151-205</u>	<u>161-206</u>	<u>161-207</u>
Solvent	--	--	--	--	--	Benzene ^(a)
Reaction Temperature, C	-196	-196	-78	8-10	8-10	8-10
Reaction Time, hr	24	58.5	112	114	31	66
Dose Rate, 10^5 rep per hr	1.7	1.7	1.6	5.1	5.1	5.1
Total Dose, 10^7 rep	0.41	0.91	1.8	5.8	1.58	3.37
Yield, per cent	Low	Low	Low	High	61.3	24.7
Description	Viscous liquid	Viscous liquid	Viscous liquid; turned brown on contact with air	Strongly gelled; turned brown on contact with air	Tacky, rubbery solid; exhibited cold-flow; transparent; colorless	Tacky, rubbery solid; exhibited cold-flow; translucent; light yellow

(a) 30 per cent by volume TFEVE in benzene.

TABLE 16. DIELECTRIC DATA FOR POLY (β -TRIFLUOROETHYL VINYL ETHER)

Sample	<u>103-202(a)</u>		<u>161-206(b)</u>	
	1	1	1	2
Molding Temperature, F	160	160	160	160
Molding Time, min	30	30	30	30
Average Sample Thickness, in.	0.0459	0.0454	0.0451	0.0451
Dielectric Constant (K)				
0.1 Kc	16.04	15.83	15.93	
1 Kc	15.38	15.06	15.18	
10 Kc	10.24	10.38	10.65	
100 Kc	6.66	6.88	7.00	
Dissipation Factor (D)				
0.1 Kc	0.0091	0.0120	0.0106	
1 Kc	0.0637	0.0626	0.0591	
10 Kc	0.2110	0.1940	0.1910	
100 Kc	0.1630	0.1560	0.1580	

(a) Catalyzed with Hi-Sil 303.

(b) Catalyzed with γ -radiation from Co⁶⁰.

Diphenyl Allyl Phosphite and Allyl Cyanide

Both of these polar-allylic materials were chosen because of the well-known inertness of this type of unsaturated compound to polymerization. If polymers could be prepared by radiation, products of high dielectric constants might be expected.

DPAP from Hooker Chemical Corporation was distilled from CaH₂ into well-flamed reaction vessels and was irradiated at 1.3×10^5 rep per hr and 8 to 10 C to a total dose of 1.55×10^7 rep and at 1.6×10^5 rep per hr, and -196 C to total doses of 1.4, 3.1, and 4.6×10^6 rep. No polymer was found in the first experiment and only trace yields, manifested by a slight cloudiness on precipitation in hexane and a very small charred residue on distilling off the monomer, were obtained from the low-temperature polymerization. Another irradiation was run at 60 C and 1.6×10^5 rep per hr to a total dose of 1×10^7 rep. An oily, low-viscosity fluid was produced in good yield.

A polymerization experiment at a high dose rate was conducted with allyl cyanide from Matheson, Coleman, and Bell after distillation from CaH₂. The monomer was irradiated at 8 to 10 C and 5.1×10^5 rep per hr to a total dose of 3.35×10^7 rep, but only a trace of residue was recovered after distilling off the unreacted monomer.

CONCLUSIONS

(1) Effect of catalysts on the dielectric properties of polymers

- (a) Chemical and radiation catalytic methods lead to polymers of similar dielectric properties. The quantities of chemical-free-radical reagents necessary to carry out the conversion of readily polymerizable monomers as exemplified by MMA are usually in the range of 0.1 to 0.5 per cent. The effect of any residue which may remain in the polymer is small and probably overshadowed by other common impurities such as residual solvent and monomers.
- (b) The conclusion stated above is supported by the evidence of a difficult-to-polymerize monomer such as EVS. Although large concentrations, up to 1.0 per cent, of chemical catalysts are required to achieve even partial conversion, there is no evidence that catalyst residues are a significant factor in determining dielectric properties.
- (c) A slight improvement of the D-values of the radiation-catalyzed over the chemically catalyzed polymers in PTFEVE seems indicated by the data. However, the differences appear to be small.

(2) Polymers of high dielectric constant

- (a) The glass transition temperatures of a polymer is a major factor in determining the dielectric properties. PCEA with polar nitrile groups at the end of six-atom side chains has a T_g above room temperature and dielectric constants of 12 to 18 at low frequencies. Similarly, the appropriate values for PTFEVE lie between 15 and 16.

PEVS, possessing the more polar sulfone group close to the backbone of the chain, is hard and brittle at room temperature and has dielectric constants mostly between 4 and 5 at these same frequencies. Similarly, the copolymers of these monomers have considerably greater dielectric constants in flexible than in rigid compositions.

(3) Polymerization and polymer properties

- (a) Methyl methacrylate is easily polymerized to any desirable molecular weight with both chemical catalysts and γ -radiation.
- (b) β -Cyanoethyl acrylate is readily polymerized in an acetonitrile solution with small concentrations of free-radical catalysts or with low radiation doses. Low monomer concentrations are preferred to minimize crosslinking through the α -hydrogen. Polymers prepared in MEK gave cloudy solutions and had considerably lower molecular weights than those prepared in acetonitrile. Benzene is a nonsolvent for the polymers. Polymers deposit on the walls of the vessel and are easily gelled.
- (c) Ethyl vinyl sulfone is highly inert to polymerization. Even at free-radical levels of 1.0 per cent, yields were seldom over 50 per cent and number-average molecular weights were around 1000 to 2000 or less. Benzene was a more effective solvent than MEK or acetonitrile. A yield above 60 per cent could be achieved in a radiation polymer by means of a high dose rate and a large total dose. An experiment at 60 C at a lower dose rate was ineffective in raising the yield. Irradiation in the solid state was unsuccessful.
- (d) The copolymerization of ethyl vinyl sulfone and β -cyanoethyl acrylate proceeded with the same difficulty as the homopolymerization of EVS. Polymers were considerably richer in CEA content than the monomer ratio, and molecular weights were somewhat higher than those of PEVS. Copolymers remained hard and brittle up to a CEA content of 60 mole per cent and only became flexible above 70 mole per cent CEA.
- (e) β -Trifluoroethyl vinyl ether can be polymerized by radiation. Exposure of the monomer in bulk to a high total dose at about 10 C and a dose rate of 5.1×10^5 rep per hr resulted in about 60 per cent conversion to a transparent, colorless, rubbery product. Low dose rates and temperatures of -78 or -196 C produced only viscous liquids.
- (f) Diphenyl allyl phosphite and allyl cyanide could not be polymerized to solid resins, though a large yield of a low-viscosity oil was obtained from DPAP. Temperatures of -196 to 60 C and dose rates of 1.3 to 5.1×10^5 rep per hr were briefly explored to high total doses.

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